

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

MITTAL LETTER TO THE UNITED STATES

JMYT-236US

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

CONCERNING A FILING UNDER 35 U.S.C. 371

To Be Assigned 09/807655

NATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/GB99/03277

04 October 1999 (04.10.99)

16 October 1998 (16.10.98)

TITLE OF INVENTION

SUBSTRATE BINDER

APPLICANT(S) FOR DO/EO/US

FONGALLAND, Dharshini Chryshantha; GASCOYNE, John Malcolm; and RALPH, Thomas Robertson

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
09/007655		PCT/GB99/03277		JMYT-236US	
21. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$970.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO				\$840.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$690.00	
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4)				\$670.00	
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)				\$96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	23 - 20 =	3	x \$18.00	\$54.00	
Independent claims	3 - 3 =	0	x \$80.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$914.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).			<input type="checkbox"/>	\$0.00	
SUBTOTAL =				\$914.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$914.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input checked="" type="checkbox"/>	\$40.00	
TOTAL FEES ENCLOSED =				\$954.00	
				Amount to be refunded	\$
				charged	\$

☒ A check in the amount of **\$954.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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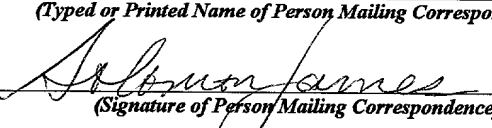
NAME _____

36,201

REGISTRATION NUMBER

April 16, 2001

DATE _____

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): Dharshini Chryshantha Fongalland et al.			Docket No. JMYT-236US	
Serial No. To Be Assigned	Filing Date Herewith	Examiner	Group Art Unit	
Invention: SUBSTRATE BINDER				
<p>I hereby certify that the following correspondence:</p> <div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> U.S. National Phase Application w/Form PTO-1390 and all of the documents listed therein </div> <p style="text-align: center;"><i>(Identify type of correspondence)</i></p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231</p> <div style="display: flex; justify-content: space-between; margin-top: 20px;"> <div style="width: 30%;"> <p><u>April 16, 2001</u></p> <p><i>(Date)</i></p> </div> <div style="width: 60%; text-align: center;"> <p>Solomon James</p> <p><i>(Typed or Printed Name of Person Mailing Correspondence)</i></p> <div style="margin: 10px 0;">  </div> <p><i>(Signature of Person Mailing Correspondence)</i></p> <p>EL751749185US</p> <p><i>("Express Mail" Mailing Label Number)</i></p> </div> </div>				
<p>Note: Each paper must have its own certificate of mailing.</p>				

09/807655 "041601"

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Dharshini C. Fongalland et al. : Art Unit:
Application No.: To Be Assigned : Examiner:
Filed: Herewith :
FOR: SUBSTRATE BINDER :

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

IN THE SPECIFICATION:

Please replace the paragraph beginning at page 5, line 14, with the following:

The substrate of the invention is suitable for use in the preparation of a composite membrane for use in a fuel cell. When for use in a fuel cell, the total thickness of the membrane is less than 200 μ m and preferably less than 100 μ m.

Please replace the paragraph beginning at page 6, line 18, with the following:

2. Perfluorinated or partially-fluorinated polymers further having aromatic rings, such as those described in PCT patent specifications numbers WO 95/08581 and WO 97/25369, which have been functionalised with SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, and/or OPO₃H₂. Also included are radiation- or chemically-grafted perfluorinated polymers, in which the perfluorinated carbon chain is activated by radiation or chemical initiation in the presence of a monomer, such as styrene, which can be functionalised to contain an ion-exchange group. Suitable perfluorinated polymers

include, for example, PTFE, fluorinated ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, tetrafluoroethylene-perfluoroalkoxy (PFA) copolymers, poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF).

IN THE CLAIMS:

Please replace claims 3-6, 8-12, 14-17, 19 and 20 with the following amended claims.

1 3. (Amended) A substrate according to claim 1, wherein the
2 fluorinated hydrocarbon polymer comprises one or more non-ion-conducting
3 polymer(s).

1 4. (Amended) A substrate according to claim 3, wherein the
2 non-ion-conducting polymer is selected from the group consisting of
3 polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP),
4 tetrafluoroethylene-ethylene (ETFE) copolymers, poly(vinylfluoride) (PVF) and
5 poly(vinylidene fluoride) (PVDF).

1 5. (Amended) A substrate according to claim 1, wherein the
2 silica comprises a colloidal silica and the polymer comprises PTFE.

1 6. (Amended) A substrate according to claim 1, wherein the
2 ratio of silica to polymer is in the range of from 95:5 % to 5:95 % based on w/w
3 solid materials in the binder mixture.

1 8. (Amended) A substrate according to claim 7 wherein the
2 ratio of silica to polymer is about 50:50 %, based on w/w solid materials in the
3 binder mixture.

1 9. (Amended) A substrate according to claim 1, wherein the
2 mixed binder is in the form of a dilute aqueous dispersion.

1 10. (Amended) A substrate according to claim 9 wherein the
2 dilute aqueous dispersion has about 10wt % solids in the aqueous solution.

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1 11. (Amended) A substrate according to claim 1, wherein the
2 fibres comprise at least one of glass or silica.

1 12. (Amended) A substrate according to claim 1, wherein the
2 fibres have a diameter in the range of from 0.1 μ m to 50 μ m.

1 14. (Amended) A membrane according to claim 13 which, when
2 dried then boiled in water undergoes less than or equal to about $\pm 16\%$ change in its
3 area.

1 15. (Amended) A process for preparing a porous substrate
2 according to claim 1, which process comprises applying an aqueous dispersion of
3 silica and a fluorinated hydrocarbon polymer to a porous matrix of wet fibres.

1 16. (Amended) A process for the manufacture of a substrate,
2 comprising the steps of

- 3 (a) dispersing fibres in water to form a slurry;
4 (b) depositing the slurry onto a mesh-bed to form a fibre
5 network;
6 (c) drying and compacting the fibre network; and
7 (d) applying, before or after step (c), a dispersion of a binder
8 comprising both silica and a fluorinated hydrocarbon
9 polymer.

1 17. (Amended) A process for the manufacture of a membrane,
2 comprising the steps of

- 3 (i) forming a porous substrate according to claim 16; and,
4 thereafter,
5 (ii) impregnating the fibre matrix substrate with a polymeric
6 material to produce a membrane.

1 19. (Amended) A membrane electrode assembly comprising a
2 composite membrane according to claim 13.

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1 20. (Amended) A fuel cell comprising a composite membrane
2 according to claim 13.

 Please add the following new claims:

1 21. (Newly Added) A membrane according to claim 14, wherein
2 said membrane undergoes less than or equal to about $\pm 10\%$ change in area.

1 22. (Newly Added) A membrane according to claim 14, wherein
2 said membrane undergoes an expansion in area of about 0 to about 6%.

1 23. (Newly Added) A process according to claim 17, wherein
2 said mixed amorphous silica fibres are randomly oriented in said porous substrate.

Respectfully submitted,



Christopher R. Lewis, Reg. No. 36,201
Attorney for Applicants

CRL/lrb

Dated: April 16, 2001

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Date of Deposit: April 16, 2001

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.



Solomon James

0980755-044601

VERSION WITH MARKINGS TO SHOW CHANGES MADEIN THE SPECIFICATION:

Specification at page 5, line 8:

The substrate of the invention is [suitably] suitable for use in the preparation of a composite membrane for use in a fuel cell. When for use in a fuel cell, the total thickness of the membrane is less than 200µm and preferably less than 100µm.

Specification at page 6, line 18:

2. Perfluorinated or partially-fluorinated polymers further having aromatic rings, such as those described in PCT patent specifications numbers WO 95/08581[, WO 95/08581] and WO 97/25369, which have been functionalised with SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, and/or OPO₃H₂. Also included are radiation- or chemically-grafted perfluorinated polymers, in which the perfluorinated carbon chain is activated by radiation or chemical initiation in the presence of a monomer, such as styrene, which can be functionalised to contain an ion-exchange group. Suitable perfluorinated polymers include, for example, PTFE, fluorinated ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, tetrafluoroethylene-perfluoroalkoxy (PFA) copolymers, poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF).

IN THE CLAIMS:

1 3. (Amended) A substrate according to claim 1 [or claim 2],
2 wherein the fluorinated hydrocarbon polymer comprises one or more non-ion-
3 conducting polymer(s).

1 4. (Amended) A substrate according to [any preceding] claim 3,
2 wherein the non-ion-conducting polymer is selected from the group consisting of
3 polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP),

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4 tetrafluorethylene-ethylene (ETFE) copolymers, poly(vinylfluoride) (PVF) and
5 poly(vinylidene fluoride) (PVDF).

1 5. (Amended) A substrate according to [any preceding] claim 1,
2 [which] wherein the silica comprises a colloidal silica[:PTFE mixed binder] and the
3 polymer comprises PTFE.

1 6. (Amended) A substrate according to [any preceding] claim 1,
2 wherein the ratio of silica to polymer is in the range of from 95:5 % to 5:95 % based
3 on w/w solid materials in the binder mixture.

1 8. (Amended) A substrate according to [claim 6 or] claim 7
2 wherein the ratio of silica to polymer is about 50:50 %, based on w/w solid
3 materials in the binder mixture.

1 9. (Amended) A substrate according to [any preceding] claim 1,
2 wherein the mixed binder is in the form of a dilute aqueous dispersion.

1 10. (Amended) A substrate according to claim 9 wherein the
2 [mixed binder is in the form of a] dilute aqueous dispersion [of] has about 10wt %
3 solids in the aqueous solution.

1 11. (Amended) A substrate according to [any preceding] claim 1,
2 wherein the fibres [comprises] comprise at least one of glass [and/or] or silica.

1 12. (Amended) A substrate according to [any preceding] claim 1,
2 wherein the fibres have a diameter in the range of from 0.1µm to 50µm.

1 14. (Amended) A membrane according to claim 13 which, when
2 [tested by the method described herein in the Examples, results in] dried then
3 boiled in water undergoes less than or equal to about $\pm 16\%$ change in its area[;
4 preferably, $\leq \pm 10\%$ area change; more preferably, in the range of from about 0 to
5 about 6% expansion].

1 15. (Amended) A process for preparing a porous substrate
2 according to [any one of claims] claim 1 [to 12], which process comprises applying
3 an aqueous dispersion of silica and a fluorinated hydrocarbon polymer to a porous
4 matrix of wet fibres.

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1 16. (Amended) A process for the manufacture of a substrate
2 [according to any one of claims 1 to 12], [which process comprises] comprising the
3 steps of

4 (a) dispersing [the] fibres in water to form a slurry;

5 (b) depositing the slurry onto a mesh bed to form a fibre
6 network;

7 (c) drying and compacting the fibre network; and

8 (d) applying, before or after step (c), a dispersion of [the] a
9 binder comprising both silica and a fluorinated hydrocarbon
10 polymer.

1 17. (Amended) A process for the manufacture of a membrane
2 [according to claim 13 or claim 14], [which process comprises] comprising the
3 steps of

4 (i) forming a porous substrate [of, preferably randomly
5 orientated individual, mixed amorphous silica fibres bound
6 with a binder by a process] according to claim 16; and,
7 thereafter,

8 (ii) impregnating the fibre matrix substrate with a polymeric
9 material to produce a membrane.

1 19. (Amended) A membrane electrode assembly comprising [a
2 substrate according to any one of claims 1 to 12 and/or] a composite membrane
3 according to claim 13 [or claim 14].

1 20. (Amended) A fuel cell comprising [a substrate according to
2 any one of claims 1 to 12 and/or] a composite membrane according to claim 13 [or
3 claim 14].

Claims 21-23 have been added.

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SUBSTRATE BINDER

The present invention relates to a substrate for a composite membrane that is of use in electrochemical devices, particularly fuel cells, and a process for the manufacture of the substrate and composite membrane.

Electrochemical cells invariably comprise an ion-conducting electrolyte and two electrodes, the anode and cathode, at which the desired electrochemical reactions take place. Electrochemical cells may be found in a range of devices, for example fuel cells, batteries, sensors, electrodialysis reactors and electrolytic reactors. They have a diverse range of applications, including the electrolysis of water, chemical synthesis, salt splitting, water purification, effluent treatment and metal finishing, among others.

A fuel cell is an energy conversion device that efficiently converts the stored chemical energy of its fuel into electrical energy. It does so by combining either hydrogen, stored as a gas or methanol, stored as a liquid or a gas, with oxygen to generate electrical power. The hydrogen or methanol is oxidised at the anode and oxygen is reduced at the cathode. Both electrodes are of the gas diffusion type. The electrolyte has to be in contact with both electrodes, and may be acidic or alkaline, and liquid or solid, in nature. In proton exchange membrane fuel cells (PEMFC), the electrolyte is a solid, ion-conducting, *i.e.* a proton-conducting, polymer membrane. The membrane is commonly based on a copolymer of perfluorosulphonic acid and tetrafluoroethylene. The combined structure formed from the membrane and the two gas diffusion electrodes is known as the membrane electrode assembly (MEA).

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Conventionally, solid ion-conducting membrane electrolytes useful in fuel cells and other devices are selected from commercially-available membranes, for example perfluorinated membranes sold under the trade names Nafion® (E I DuPont de Nemours and Co.), Aciplex® (Asahi Chemical Industry) and Flemion® (Asahi Glass KK). For application in the PEMFC, they are typically below 200µm in thickness to ensure a high level of ionic conductivity. One of the problems experienced with these conventional proton-conducting

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membranes used for PEM fuel cell construction, is the dimensional changes that occur as the level of water content (hydration) of the membrane changes. This is a particular problem during fabrication of the MEA, in which the membrane is typically in a highly hydrated form, as the stresses produced by changes in hydration during the conventionally-employed thermal bonding process can be large enough to break the bond between either the catalyst and the membrane or the catalyst and the substrate. Furthermore, these dimensional changes lead to considerable difficulties in handling membranes during the fabrication of MEAs, particularly large area MEAs in excess of, for example, 500cm². The thinner the membrane, the more difficult the handling becomes.

Yet further, it is current practice that most MEAs are fabricated as single items, with areas of, for example, 500cm² in a batch-type process. It is critical to the successful commercialisation of the PEMFC that lower cost, high volume, MEA manufacturing processes be developed in the future, such as a continuous fabrication process. The problem of dimensional change of the membrane with changes in hydration on a continuous process, which may employ membranes of many hundreds of metres in length, would then be an even more serious issue, and would add significant complications and cost to the manufacturing process.

With thicker types of membrane (*e.g.* >350µm) developed for other applications, it has been possible to incorporate 'macro reinforcing materials, such as woven polytetrafluoroethylene (PTFE), to minimise such dimensional changes. However, these thicker materials have too low an ionic conductivity to be of use in the PEMFC. US patent 5,547,551 describes the fabrication of ultra-thin reinforced membranes, below 25µm in thickness, comprising proton-exchange polymeric material incorporated into an expanded porous PTFE membrane. According to Kolde *et al*, *Electrochemical Society Proceedings* 95 (23) 193-201 (1995), these reinforced membranes have considerably improved dimensional stability compared to the conventional non-reinforced membranes, such as Nafion® 117 which shows shrinkage upon dehydration from the hydrated state. However, such materials have a higher specific resistance (*i.e.* lower ionic conductivity) by a factor of at least two than a non-reinforced pure proton-conducting membrane such as Nafion® 117.

The higher specific resistance of the above reinforced membranes means that, in practice, they must be much thinner than the equivalent pure proton-conducting membrane to maintain the same overall conductivity and thus cell performance. However, reducing the thickness of the membrane reduces the advantages that a reinforced membrane can provide.

- 5 For example, there is a limit to the extent to which the thickness of the membrane can be reduced, since the durability and longevity can also decrease, and reactant gas cross-over through the membrane is more liable to occur, leading to a reduction in cell performance. Furthermore, the problems associated with dimensional stability and handling for MEA fabrication can be exacerbated with thinner membranes.

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There is therefore the need to overcome the disadvantages of conventional pure and prior art reinforced membranes, by providing a novel composite ion-exchange membrane having a significantly improved dimensional stability and satisfactory handling without compromising the ionic conductivity and reactant gas cross-over parameters. Furthermore, there is a need to take account of the likely process(es) by which the membrane would be manufactured in the future in choosing an appropriate membrane composition. In particular, with the prospect of continuous fabrication processes mentioned above, it is not only the structure of the membrane that may be critical. In a composite membrane generally comprising a porous substrate of fibres impregnated, coated or otherwise associated with the ion-conducting polymer (*e.g.* Nafion®), the strength and stability of the substrate itself would be an important factor.

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Accordingly, the present invention provides a substrate, suitable for the preparation of a composite membrane, which substrate comprises a porous matrix of fibres, characterised in that the fibres are bound with both silica and a fluorinated hydrocarbon polymer.

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The silica is preferably a colloidal silica binder, more preferably in the form of a colloidal aqueous solution, such as is available from DuPont, Antwerp under the trade name Syton® T40AS or Ludox®. Alternatively, a silica powder, such as is available under the Cab-O-Sil™ name from the Cabot Corporation, could be dispersed in water to produce a suitable solution.

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The fluorinated hydrocarbon polymer includes non-ion-conducting polymers, such as polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, poly(vinylfluoride) (PVF) and poly(vinylidene fluoride) (PVDF), but preferably PTFE.

5

Preferably, the binders are mixed before application. Most preferred is a colloidal silica:PTFE mixed binder.

The ratio of silica to polymer may be in the range of from 95:5% to 5: 95%, and is preferably in the range of 90:10% to 10:90%, such as 70:30% to 30:70%, *e.g.* 50:50%. Most preferred is when the two components are present in approximately equal amounts, based on w/w solid materials in the binder mixture.

Hence, especially preferred is a substrate comprising fibres characterised by being bound together by colloidal silica:PTFE (about 1:1).

The mixed binder for use in preparing the substrate according to the present invention is preferably in the form of a dilute aqueous dispersion, such as a 1-30%, preferably a 5-20% *e.g.* about 10wt% solids in the aqueous solution. More preferably, the binder is applied during the process for forming the matrix of fibres whilst the fibres are still wet, so that the binder replaces the water as the latter is shed. Thereafter, the bound fibres are dried.

Accordingly, the present invention further provides a process for preparing a porous substrate as defined herein, which process comprises applying an aqueous dispersion of silica and a fluorinated hydrocarbon polymer to the porous matrix of fibres prior to drying thereof.

A broad range of fibres is suitable for use in this aspect of the invention. For example, glass, polymer (but preferably not PTFE or polyethylene), silica, carbon or metal fibres may be used. In the case of carbon or metal, these fibres would need to be electrically insulated prior to forming the porous substrate into a membrane, as further defined below. Preferably, glass and/or silica fibres, or mixtures thereof are used.

The fibres within the substrate are preferably randomly orientated in the x and y direction (in-plane), producing a two-dimensional isotropic structure. Additionally, random orientation in the z direction (through-plane) can be introduced with the inclusion of very short fibres, typically lengths of less than or equal to 0.2mm or very fine fibres, typically of diameters less than or equal to $1\mu\text{m}$. The fibres typically have a diameter in the range of from $0.1\mu\text{m}$ to $50\mu\text{m}$, preferably $0.2\mu\text{m}$ to $20\mu\text{m}$ and, more preferably, about $0.4\mu\text{m}$ to $9\mu\text{m}$. The fibres typically have lengths in the range of from 0.05mm to 300mm, suitably 0.5mm to 150mm, preferably 1mm to 50mm and, more preferably, about 6mm to 20mm.

The porous substrate typically has at least 50%, suitably at least 75%, of the individual pore sizes being greater than $1\mu\text{m}$ in at least one direction, although a porous substrate wherein some of the pores are less than $1\mu\text{m}$ in all directions is within the scope of the invention.

The substrate of the invention is suitably for use in the preparation of a composite membrane for use in a fuel cell. When for use in a fuel cell, the total thickness of the membrane is less than $200\mu\text{m}$ and preferably less than $100\mu\text{m}$.

For its use in the preparation of a composite membrane, the substrate is preferably associated with an ion-conducting polymer. Accordingly, the present invention further provides a composite membrane comprising a porous substrate of fibres and at least one ion-conducting polymer, characterised in that the substrate comprises fibres that are bound with both silica and a fluorinated hydrocarbon polymer.

The substrates according to the present invention, when used as a membrane by the incorporation of an ion-conducting polymer therein, produce a surprising effect on the dimensional stability of the membrane when subject to full hydration conditions. Accordingly, when tested by the method described hereinafter in the Examples, the dimensional changes in membranes based on the substrates according to the present invention result in less than or equal to about $\pm 16\%$ change in their areas. Preferably, the membranes show $\leq \pm 10\%$ area change. More preferably, the membranes show in the range of from about 0 to about 6% expansion when tested according to the method described herein.

For PEM fuel cell applications, the ion-conducting polymer is a proton-conducting polymer, examples of such polymers being well known to those skilled in the art. More than one proton-conducting polymer may be present and/or a non-proton-conducting polymer may also be included in the novel membrane of the present invention.

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Proton-conducting polymers suitable for use in the present invention include, but are not limited to:

1. Polymers having a substantially fluorinated, straight or branched carbon chain, further having acidic groups or derivatives thereof selected from the following acids: sulphonic, carboxylic, phosphonic, phosphoric, and/or mixtures thereof. Perfluorinated polymers include Nafion®, Flemion® and Aciplex®, which are commercially available from E I DuPont de Nemours (c.f. US patents specifications numbers 3,282,875; 4,329,435; 4,330,654; 4,358,545; 4,417,969; 4,610,762; 4,433,082 and 5,094,995); Asahi Glass KK and Asahi Chemical Industry, respectively. Other such polymers include those disclosed in US patents specification numbers 5,595,676 and 4,940,525.

2. Perfluorinated or partially-fluorinated polymers further having aromatic rings, such as those described in PCT patents specifications numbers WO 95/08581, WO 95/08581 and WO 97/25369, which have been functionalised with SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , and/or OPO_3H_2 . Also included are radiation- or chemically-grafted perfluorinated polymers, in which the perfluorinated carbon chain is activated by radiation or chemical initiation in the presence of a monomer, such as styrene, which can be functionalised to contain an ion-exchange group. Suitable perfluorinated polymers include, for example, PTFE, fluorinated ethylene-propylene (FEP), tetrafluoroethylene-ethylene (ETFE) copolymers, tetrafluoroethylene-perfluoroalkoxy (PFA) copolymers, poly(vinyl fluoride) (PVF) and poly (vinylidene fluoride) (PVDF).

3. Fluorinated polymers, such as those disclosed in European patent specifications numbers EP 0 331 321 and EP 0345 964, having pendant saturated cyclic groups and at least one ion-exchange group that is linked to the polymeric chain through the cyclic group.

4. Aromatic polymers, such as those disclosed in European patent specification number EP 0 574 791 and US patent specification number 5 438 082, for example, sulphonated polyaryletherketones. Also polyether sulphones, which can be chemically grafted with a polymer with ion-exchange functionality, such as those disclosed in PCT patent specification number WO 94/16002.

5. Non-fluorinated polymers, including those disclosed in US patent specification number 5 468 574, for example, hydrocarbons such as styrene-(ethylene-butylene)-styrene, styrene-(ethylene-propylene)-styrene and acrylonitrile-butadiene-styrene co- and ter-polymers, where the styrene components are functionalised with sulphonate, phosphoric and/or phosphonic groups.

6. Nitrogen-containing polymers, including those disclosed in US patent specification number 5 599 639, for example, polybenzimidazole alkyl sulphonic acids and polybenzimidazole alkyl or aryl phosphonates.

7. Any of the above polymers wherein the ion-exchange group is replaced with a sulphonyl chloride (SO_2Cl) or sulphonyl fluoride (SO_2F) group, thereby rendering the polymers melt-processable. The sulphonyl fluoride polymers may form part of the precursors to the ion-exchange membrane or may be arrived at by subsequent modification of the ion-exchange membrane. The sulphonyl halide moieties can be converted to sulphonic acid using conventional techniques such as, for example, hydrolysis.

Other non-ion-conducting polymeric materials may be used in addition to the one or more ion-conducting or proton-conducting polymers. Examples of such non-ion-conducting polymers include fluorinated polymers, *e.g.* PTFE, FEP, PVDF, Viton®, and hydrocarbon types *e.g.* polyethylene, polypropylene and polymethylmethacralate.

Other ion-conducting polymeric materials which are not proton-conducting may be used in addition to, or in place of, a proton-conducting polymer. Such polymers can be used for applications requiring a bipolar membrane or a completely anion exchange membrane.

Anion exchange polymers are generally based on quaternary ammonium groups, rather than the fixed sulphonic acid groups in proton conducting polymers. These include, for example, the tetra-alkyl ammonium group ($-N^+R_3$) and the quaternary ammonium centre in Tosflex® membranes ($-N(R_1)(CH_2)_yN^+(R_3)$) supplied by Tosoh. However, it can be envisaged that all of the proton exchange polymers described above could have anion exchange equivalents.

The polymer is suitably applied to the coated fibres (substrate) in the form of a solution, the solvents of which may be either organic or aqueous based. Solvents of all of the above polymers may include or may be modified to include, water, methanol and/or other aliphatic alcohols, ethers, acetone, tetrahydrofuran (THF), n-methylpyrrolidone (NMP), dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAc), or protonic solvents such as sulphuric acid or phosphoric acid, and/or mixtures of the above. However, it has been found that an essentially aqueous solution of the polymer as described in EP 0 731 520 is preferred.

A flexible free-standing, dimensionally stable composite membrane is produced by using the substrate of the present invention, resulting in greater handlability. The membrane of the invention is therefore also more amenable to high volume, continuous production processes, as described hereinafter. The high dimensional stability of the membrane enables thinner membranes to be produced, which are more amenable to higher volume MEA manufacturing processes than are current membranes, at similar thicknesses. Current materials show very large dimensional changes with changes in the levels of water content that occur during MEA fabrication, and are therefore very difficult to handle during the MEA fabrication process.

In a further embodiment, a laminated membrane comprising more than one polymer-containing layer is provided, at least one layer of which is a composite membrane of the invention. Where a laminated membrane is formed that comprises more than one composite membrane layer of the invention, each layer may comprise either the same or different types of fibres and porous substrates, and also the same or different types of polymeric material embedded within the porous substrate of each composite membrane layer. Using such a

laminated structure, it is possible, for example, to tailor the properties of the laminate membrane opposed to the anode and cathode sides in the MEA of a proton exchange membrane fuel cell, for example, to improve water management in the fuel cell, or to be able to use lower cost proton-conducting polymers to form a substantial part of the laminate membrane.

Composite membranes comprising the substrate of the present invention are suitable for low cost manufacture, and the substrates and membranes may be manufactured by:

- (i) forming a porous substrate of, preferably randomly orientated individual, especially preferably mixed amorphous silica, fibres bound together with silica and a fluorinated hydrocarbon polymer by adapting a continuous manufacturing process, which for example may be based on wet lay processes such as those employed in paper-making, or dry lay processes employed, for example, to produce non-woven fabrics and felts; and, optionally, thereafter,
- (ii) impregnating the fibre matrix substrate with the polymeric material to produce a membrane. This can be done by any number of coating processes such as printing, rolling, K-bar, doctor blade methods, spraying or thin-film casting.

For example, in a process based on a paper-making technology to prepare a composite membrane, the fibres are dispersed in water to form a dilute slurry and thereafter a continuous structure is formed by the controlled deposition of said slurry onto a moving mesh bed, dewatering the solids, and drying and compacting the fibre network. The solution containing the dispersion of the silica plus fluorinated hydrocarbon polymer binder material can be applied either at the wet end of the process, *i.e.* before the drying stage, or after the network has been dried. This is followed by nip roller coating of the substrate to fill it with a solution of the ion-conducting polymeric material, and further compaction and drying of the membrane under a suitable time, temperature and pressure regime to produce the final thin film or sheet of fibre/polymer composite membrane.

A major advantage of using a continuous manufacturing method, such as a

conventional paper making technique, is that the composite membrane is easily manufactured in a fewer number of steps than prior art composite membranes, thus making it more cost-effective and commercially viable. The membrane may also be produced in continuous lengths of many metres and widths of equal to or greater than one metre. A further advantage is that it is possible to combine a membrane of the present invention with one or more electrode layers as described in European patent specification number EP 0 791 974 to form a membrane electrode assembly at the same rate as each individual component could be produced.

The present invention also relates to a membrane electrode assembly and a method for the manufacture thereof, wherein the composite membrane is one according to the present invention. A still further aspect of the present invention relates to a fuel cell and a method for the manufacture thereof, which fuel cell comprises a composite membrane of the present invention.

The present invention is not limited to the use of the composite membrane in a fuel cell and any electrochemical device which comprises a composite membrane of the invention is within the scope.

The present invention will now be described by way of example only which is not intended to be limiting thereof.

EXAMPLE 1: PREPARATION OF MIXED GLASS FIBRES/MIXED BINDER SUBSTRATE

A mixture of chopped glass fibres (12mm Schueller strand from Johns Manville, Insulation Group, PO Box 5108, Denver, CO, USA) (0.18g) and glass microfibre (Type 608 from Evanite Fibre Corporation, Corvallis, Oregon, USA) (0.37g) were dispersed with mixing, in water (3000ml). A non-woven matrix was fabricated from the resulting mixture in a single-step process, based on the principles of paper-making technology, as a sheet size of 855cm² (33cm diameter) in a sheet former (design based on standard SCA Sheet former from AB

Lorentzen & Wettre, Box 4, S-163 93 Stockholm, Sweden).

The fibre sheet, as formed on the wire and whilst still wet, was sprayed with a binder solution comprising a 10wt% aqueous dispersion of polytetrafluoroethylene (Teflon GP1®; ICI Chemicals and Polymers Ltd, PO Box 4, Thornton, Cleveleys, Blackpool, FY5 4QD) and a 10wt% solution of colloidal silica (Syton® T40AS; DuPont Speciality Chemicals, Havennummer 500, Wilmington Straat, 2030 Antwerp, Belgium) in a 1:1ratio to give a loading of 0.45g of the Teflon/silica mixture. The sheet was removed from the wire and air dried at 150°C, then fired in air at 280°C.

EXAMPLE 2: PREPARATION OF SILICA MICROFIBRE/MIXED BINDER SUBSTRATE

A non-woven matrix was fabricated according to the method of Example 1, but using silica microfibre (Q fibre, type 106 from Johns Manville, Insulation Group, PO Box 5108, Denver, CO, USA) (0.6g). The fibre sheet, as formed on the wire and whilst still wet, was sprayed with the mixed binder solution described in Example 1 to give a loading of 0.68g of the Teflon/silica mixture. The sheet was removed from the wire and air dried at 150°C, then fired in air at 280°C.

EXAMPLE 3: PREPARATION OF MIXED AMORPHOUS SILICA/MIXED BINDER SUBSTRATE

A mixture of chopped silica fibres (Type QC9/33-20mm from Quartz et Silice BP 521-77794 Nemours, Cedex, France) (0.18g) and silica microfibre (Q fibre, type 106 from Johns Manville, Insulation Group, PO Box 5108, Denver, CO, USA) (0.37g) were dispersed with mixing, in water (3000ml). A non-woven matrix was fabricated according to the method of Example 1.

The fibre sheet, as formed on the wire and whilst still wet, was sprayed with the mixed binder solution described in Example 1 to give a loading of 0.27g of the Teflon/silica mixture.

The sheet was removed from the wire and air dried at 150°C, then fired in air at 280°C.

COMPARATIVE EXAMPLES: Nafion® 1135, 115 & 117 Membranes

5 **Nafion® membrane type 1135** (produced by E I DuPont de Nemours, Polymer Products Department, Fayetteville, NC, USA) was used as received. A 10x10cm square was cut from the bulk membrane. A measurement of the membrane's mass was taken before the sample was placed in a sealable polyethylene bag of known weight. With the bag seal open, the membrane was dried overnight (~16 h) at 40°C under vacuum (~10mbar). After releasing
10 the vacuum, the bag was quickly sealed before being weighed. [Mass loss from the membrane and bag together was adjusted for the average mass loss from three identical bags containing no membrane]. Lengths in the x and y directions were measured whilst the dried membrane was still in the sealed bag to establish the dehydrated dimensions.

15 The membrane was placed in 2 litres of de-ionised water, heated to boiling and maintained at boiling for 90 minutes. The membrane was then removed from the de-ionised water and the excess surface water removed by blotting with filter paper. The x and y dimensions were then measured using the same procedure as before.

20 **Nafion® membranes types 115 and 117** (also produced by E I DuPont de Nemours, Polymer Products Department, Fayetteville, NC, USA) were also used as received. A 10x10cm square was cut from each bulk membrane and treated according to the above procedure.

25 The dimensional changes and area change for each comparative membrane are recorded in Table 1.

**EXAMPLE 4: PREPARATION OF TRIPLE LAMINATE MEMBRANES USING
SUBSTRATE OF EXAMPLE 1**

The non-woven mixed glass fibre/mixed binder matrix prepared according to Example 1 was placed on a sheet of sintered PTFE and a solution of perfluorosulphonic acid (Nafion[®] produced by E I DuPont de Nemours) in the aqueous form as described in EP 731 520 was applied to the fibre matrix. The structure was filled with the aqueous Nafion[®] to achieve a total solid Nafion[®] loading of 7.05mg/cm².

A further two sheets were prepared in the same fashion. The three sheets were placed on top of each other and sandwiched between two thin, non-porous PTFE sheets. The sandwich was pressed at 90 to 100psig (710-780kPa) for six minutes at 177°C to produce a triple laminate membrane.

A 10x10cm square was cut from the bulk membrane and treated by the same procedure as described in the Comparative Examples. The results are recorded in Table 1.

**EXAMPLE 5: PREPARATION OF TRIPLE LAMINATE MEMBRANES USING
SUBSTRATE OF EXAMPLE 2**

The non-woven silica fibre/binder matrix prepared according to Example 2 was treated according to the method and materials of Example 4 (total solid Nafion[®] loading of 7.24mg/cm²) to produce a triple laminate membrane, whose results also appear in Table 1.

**EXAMPLE 6: PREPARATION OF SINGLE SHEET MEMBRANES USING
SUBSTRATE OF EXAMPLE 1**

A single sheet of the non-woven mixed silica fibre matrix with the sprayed alcoholic Nafion[®] binder was formed as described in Example 1 and filled with a solution of perfluorosulphonic acid (Nafion[®] produced by E I DuPont de Nemours) in the aqueous form as described in EP 731 520 to achieve a total solid Nafion[®] loading of 7.24mg/cm².

The sheet was sandwiched between two thin, non-porous PTFE sheets. The sandwich was pressed at 90 to 100psig (710-780kPa) for six minutes at 177°C to produce a membrane.

A 10x10cm square was cut from the bulk membrane and treated by the same procedure as described in the Comparative Examples. The results are recorded in Table 1.

**EXAMPLE 7: PREPARATION OF SINGLE SHEET MEMBRANES USING
SUBSTRATE OF EXAMPLE 2**

The non-woven silica fibre/binder matrix prepared according to Example 2 was treated according to the method and materials of Example 6 (total solid Nafion® loading of 7.04mg/cm²) to produce a membrane whose results also appear in Table 1.

TABLE 1

MIXED BINDER ON FIBRE NETWORKS

Example		Fibre type	Binder Type	Dimensional Changes		
				x (%)	y (%)	z (%)
CP	Nafion® 1135	N/A	N/A	+4.1	+25.0	+30.0
CP	Nafion® 115	N/A	N/A	+15.8	+20.5	+39.0
CP	Nafion® 117	N/A	N/A	+13.4	+22.5	+39.0
4	triple laminate	mixed glass fibres	1:1 colloidal silica/PTFE	+8.0	+7.0	+16.0
5	single sheet	mixed glass fibres	1:1 colloidal silica/PTFE	+2.5	+3.0	+5.6
6	triple laminate	quartz microfine fibre	1:1 colloidal silica/PTFE	+6.0	+4.0	+10.0
7	single sheet	quartz microfine fibre	1:1 colloidal silica/PTFE	0.0	0.0	0.0

CLAIMS

CLAIMS

1. A substrate, suitable for the preparation of a composite membrane, which substrate comprises a porous matrix of fibres, characterised in that the fibres are bound with a binder comprising both silica and a fluorinated hydrocarbon polymer.
2. A substrate according to claim 1, wherein the silica comprises a colloidal aqueous solution, or a silica powder dispersed in water.
3. A substrate according to claim 1 or claim 2, wherein the fluorinated hydrocarbon polymer comprises one or more non-ion-conducting polymer(s).
4. A substrate according to any preceding claim wherein the non-ion-conducting polymer is selected from the group consisting of polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), tetrafluorethylene-ethylene (ETFE) copolymers, poly(vinylfluoride) (PVF) and poly(vinylidene fluoride) (PVDF).
5. A substrate according to any preceding claim, which comprises a colloidal silica:PTFE mixed binder.
6. A substrate according to any preceding claim, wherein the ratio of silica to polymer is in the range of from 95:5% to 5:95% based on w/w solid materials in the binder mixture.
7. A substrate according to claim 6 wherein the ratio of silica to polymer is in the range of from 70:30% to 30:70% based on w/w solid materials in the binder mixture.
8. A substrate according to claim 6 or claim 7 wherein the ratio of silica to polymer is about 50:50%, based on w/w solid materials in the binder mixture.

9. A substrate according to any preceding claim, wherein the mixed binder is in the form of a dilute aqueous dispersion.
10. A substrate according to claim 9 wherein the mixed binder is in the form of a dilute aqueous dispersion of about 10wt% solids in the aqueous solution.
11. A substrate according to any preceding claim, wherein the fibres comprises glass and/or silica.
12. A substrate according to any preceding claim, wherein the fibres have a diameter in the range of from 0.1 μ m to 50 μ m.
13. A composite membrane comprising a porous substrate of fibres and at least one ion-conducting polymer, characterised in that the porous substrate comprises fibres that are bound with both silica and a fluorinated hydrocarbon polymer.
14. A membrane according to claim 13 which, when tested by the method described herein in the Examples, results in less than or equal to about $\pm 16\%$ change in its area; preferably, $\leq \pm 10\%$ area change; more preferably, in the range of from about 0 to about 6% expansion.
15. A process for preparing a porous substrate according to any one of claims 1 to 12, which process comprises applying an aqueous dispersion of silica and a fluorinated hydrocarbon polymer to a porous matrix of wet fibres.
16. A process for the manufacture of a substrate according to any one of claims 1 to 12, which process comprises
- dispersing the fibres in water to form a slurry;
 - depositing the slurry onto a mesh bed to form a network;
 - drying and compacting the fibre network; and
 - applying, before or after step (c), a dispersion of the binder.

17. A process for the manufacture of a membrane according to claim 13 or claim 14, which process comprises

- 5 (i) forming a porous substrate of, preferably randomly orientated individual, mixed amorphous silica fibres bound with a binder by a process according to claim 16; and, thereafter,
- (ii) impregnating the fibre matrix substrate with a polymeric material to produce a membrane.

10 18. A process according to claim 17, wherein step (ii) is carried out by nip roller coating of the substrate to fill it with a solution of ion-conducting polymeric material, and further compaction and drying of the membrane.

15 19. A membrane electrode assembly comprising a substrate according to any one of claims 1 to 12 and/or a composite membrane according to claim 13 or claim 14.

20. A fuel cell comprising a substrate according to any one of claims 1 to 12 and/or a composite membrane according to claim 13 or claim 14.

09807655-041601

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SUBSTRATE BINDER,

the specification of which is attached hereto unless the following box is checked:



was filed on October 4, 1999 as

United States Application Number or PCT International Application Number PCT/GB99/03277

and was amended by Preliminary Amendment filed along with the application (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Not Claimed

9822571.7

Great Britain

16 October 1998

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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3-0
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